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Compound Effect of $CaCO_3$ and $CaSO_4 \cdot 2H_2O$ on the Strength of Steel Slag - Cement Binding Materials

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In this study, we replaced 30% of the cement with steel slag to prepare binding material; additionally, small amounts of $CaCO_3$ and $CaSO_4 \cdot 2H_2O$ were added. This was done to study the compound effect of $CaCO_3$ and $CaSO_4 \cdot 2H_2O$ on the strength of steel slag-cement binding materials. The hydration degree of the steel slag cementitious material was analyzed by XRD, TG and SEM. The results showed that the optimum proportions of $CaCO_3$ and $CaSO_4 \cdot 2H_2O$ were 3% and 2%, respectively. Compared with the steel slag-cement binders without adding $CaCO_3$ and $CaSO_4 \cdot 2H_2O$, the compressive strength increased by 59.9% at 3 days and by 17.8% at 28 days. Acting as the nucleation matrix, $CaCO_3$ could accelerate the hydration of C_3S. In addition, $CaCO_3$ was involved in the hydration reaction, generating a new hydration product, which could stably exist in a slurry. Meanwhile, $CaSO_4 \cdot 2H_2O$ could increase the number of AFt. The compound effect of $CaCO_3$ and $CaSO_4 \cdot 2H_2O$ enhanced the intensity of steel slag-cement binding materials and improved the whole hydration behavior.

Key *words: $CaCO_3$, $CaSO_4 \cdot 2H_2O$, Steel slag, Binding materials, Strength*

1 Introduction

Steel slag is a by-product in steel production, which makes up approximately 10~15% of crude steel output [1]. At present, approximately 80 million tons of steel slag is discharged every year in China [2]; however, the current utilization rate of steel slag in China is only 22%, which is far behind developed countries such as the USA, Japan, Germany and France, of which the rates have been close to 100% [3]. The wasted steel slag occupies a large area of land and results in many serious environmental problems. Therefore, it is imperative to find effective ways to utilize steel slag. The main reason leading to the limited utilization of steel slag is that it contains volatile ingredients and has poor stability. Approximately 70% of China's steel slag is converter steel slag, the chemical and mineral composition of which is similar to that of Portland cement clinker with gelling properties. Therefore, this steel slag has great potential for application in cement.

Steel slag can show good cementitious behaviors with a chemical excitation agent and using the steel slag to replace part of cement can prepare gelling materials that satisfy the mechanical properties and durability of the specific requirements. However, when 30% of cement is replaced by steel slag, similar to other binding materials, the strength of the cement has a clear tendency to decrease. Therefore, to increase the application of steel slag as a mineral admixture for binding materials, it is necessary to weaken its negative effect on the strength and enhance its ability to improve the hydration behavior of cementitious material. The hydration performance of cement with $CaCO_3$ added has been studied and discussed both in China and abroad [4-10]. Unlike other pozzolanic mineral powder, $CaCO_3$ can accelerate the hydration of cement, improve the early strength, and change the rheology of fresh concrete, and so on. However, no consistent conclusion has been drawn regarding the mechanism of $CaCO_3$-cement gelling materials. Some scholars think $CaCO_3$ possesses hydration activity [11-14], whereas others disagree [15,16]. On the basis of the above research, the mechanism of influence of a $CaCO_3$ admixture on steel slag-cement binding materials in which the steel slag-to-cement ratio of the blended mineral admixture was 3:7(mass ratio) is discussed in this paper. In addition, $CaSO_4 \cdot 2H_2O$ was also added to the gelling system as an excitation agent. The experiments indicate that under the joint action of $CaCO_3$ and $CaSO_4 \cdot 2H_2O$, the early and late compressive strength of steel slag-cement binding materials markedly increased. Published papers concerned with this research are scarce.

2 Experimental methods

2.1 Raw materials

Cement: Portland cement with a strength grade of 42.5 that complies with the Chinese National Standard GB175-2007 was used.

Steel slag: Treated with hot stuffy process, BOF steel slag was obtained from the Xin Yu Iron and Steel Company of China. The chemical compositions of the cement and the steel slag are listed in Table1.

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Table 1 Chemical compositions of the cement and steel slag

Sample	Composition w/%							
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	FeO	Na_2O	SO_3
Cement	21.86	4.25	2.66	63.59	2.19	-	0.14	2.70
Steel Slag	11.76	1.56	11.95	49.92	7.63	8.54	-	-

2.2 Sample preparation and test methods

2.2.1 Compressive strength of mortar

To assess the influence of $CaCO_3$ and $CaSO_4 \cdot 2H_2O$ on the compressive strength of blended steel slag–cement mortar, mortar bars (4-4-16 cm) were prepared by adopting a binder-to-sand ratio of 1:3 (mass ratio) and a water-to-binder ratio of 0.50. The steel slag-to-cement ratios of the blended mineral admixture were 3:7(mass ratio), and different ratios of the additive agent (1%, 2%, 3%, 4%, 5% $CaCO_3$ by mass; 0.5%, 1%, 1.5%, 2%, 2.5% $CaSO_4 \cdot 2H_2O$ by mass) were adopted. The mortars were first cured in a fog room at 20°C and 95% relative humidity for 1 day and then were stripped from their molds and placed in 20°C water until testing. At 3, 7 and 28 days, the compressive strengths were measured, and then the appropriate proportion of $CaCO_3$ and $CaSO_4 \cdot 2H_2O$ were determined to join together in a composite gelling material. The total dosage of $CaCO_3$ and $CaSO_4 \cdot 2H_2O$ was limited to no more than 5% to prepare the mortar specimen. The compressive strengths were measured in accordance with Chinese National Standard GB/T17671-1999.

2.2.2 Preparation of mud purification

Mud purification was conducted in 10-ml one-time centrifugal pipes, which were sealed and cured under standard conditions. At the stipulated age, the samples were broken, and the middle pieces were removed and then immersed in absolute ethyl alcohol to terminate the hydration process.

3 Results and discussion

3.1 The mineral compositions of Xin Yu steel slag

As Fig. 1 shows, the main mineral composition of Xin Yu steel slag includes: C_3S, C_2S, C_4AF, $C_{12}A_7$, $Ca_2Al_2Si_3O_{17}$, RO phase, a small amount of $Ca(OH)_2$ and Fe_3O_4.

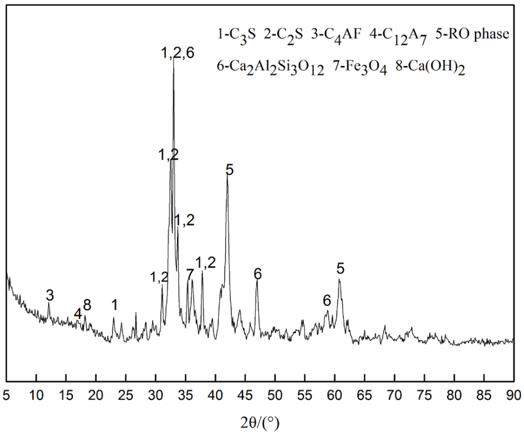


Fig. 1. XRD pattern of Xin Yu hot stuffy steel slag.

3.2 Effect of $CaCO_3$ on the strength of steel slag-cement binding materials

In the experiments, the flexural strength and compressive strength of the cementitious materials displayed the same changeable tendency. Therefore, only changes in the compressive strength are described in detail.

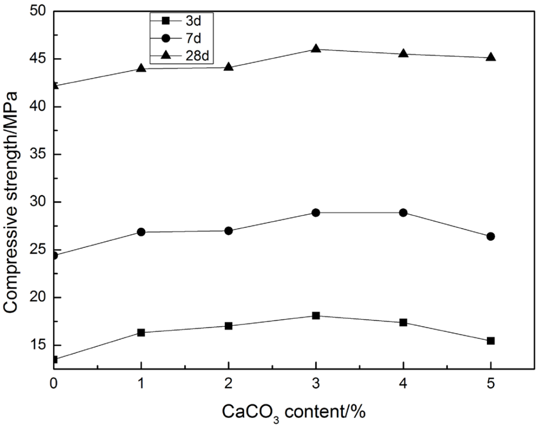


Fig. 2. Compressive strength of steel slag-cement binders with different $CaCO_3$ contents.

Fig. 2 shows the influence of different $CaCO_3$ dosages on the compressive strength of mortar. With increasing $CaCO_3$ content, the mortar's compressive strength initially increases and then decreases gradually. The optimum proportion of $CaCO_3$ is 3%. The effect of $CaCO_3$ on the steel slag-cement binding materials is mainly displayed in three aspects: First, $CaCO_3$ can serve as the nucleation substrate of hydrated silicate calcium (C - S - H), thereby reducing the nucleation barrier and promoting the hydration degree of the complex binder [17]. Second, $CaCO_3$ can react with tricalcium aluminate (C_3A) to form single-carbon hydrated calcium aluminate ($Ca_4Al_2O_6 \cdot CO_3 \cdot 11H_2O$), which can stably exist in the slurry; Third, $CaCO_3$ has a physical filling effect in the early ages, which is also the reason why it has a significant positive effect on the early-age strength of the mortar [18].

3.3 Effect of $CaSO_4 \cdot 2H_2O$ on the strength of steel slag-cement binding materials

Fig. 3 shows the influence of different $CaSO_4 \cdot 2H_2O$ dosages on the compressive strength of mortar. At 3 days, it is very obvious that the compressive strength of mortar containing $CaSO_4 \cdot 2H_2O$ increases more quickly than that of mortar without it, whereas at 28 days, the compressive strength of $CaSO_4 \cdot 2H_2O$ is very similar to or slightly higher than that of the pure steel-slag cement mortar. It is concluded that the optimum proportion of $CaSO_4 \cdot 2H_2O$ is 2%. The influence mechanism of $CaSO_4\cdot 2H_2O$ on improving the impressive strength of steel slag-cement binding materials is as follows:

$$3CaO\cdot Al_2O_3 + 3(CaSO_4.2H_2O) + 26H_2O \rightarrow 3CaO\cdot Al_2O_3\cdot 3CaSO_4.32H_2O\ (AFt) \tag{1}$$

A balanced amount of ettringite (AFt) can increase the density of make cement stone, but too many AFt crystals can loosen the paste structure, as there is not enough hydration gel to connect them in time. In addition, excessive AFt results in uneven force of internal and external force, which may increase the risk of expansionary destruction.

3.4 Compound Effect of $CaCO_3$ and $CaSO_4\cdot 2H_2O$ on the strength of steel slag-cement binding materials

Fig. 4 shows the compressive strengths of three different types of gelling materials at ages of 3,7 and 28 days. The gelling material with 100% cement is named PO; that of 30% steel slag+70% cement is PS; that of 30% steel slag+70% cement+3% $CaCO_3$+2% $CaSO_4\cdot 2H_2O$ is PSC. Compared with PS, the compressive strength of PSC at 3 days is increased by 59.9%, and that at 28 days is increased by 17.8%. The synergy of $CaCO_3$ and $CaSO_4\cdot 2H_2O$ makes the overall strength of the composite slurry increase more. This synergy is mainly because the presence of $CaCO_3$ can inhibit the conversion of ettringite (AFt) into the single type sulfur aluminate (AFm) [19], since $CaCO_3$ reacts with C_3A, generating a single carbon aluminate ($Ca_4Al_2O_6\cdot CO_3\cdot 11H_2O$); therefore, when $CaSO_4\cdot 2H_2O$ consumption has finished, the remaining C_3A in system that is intended for AFt to react will reduce relatively, as a result of inhibiting the conversion from AFt to Afm, thus improving the strength of the complex binder. Compared with the single-sulfur aluminate, the single-carbon aluminate has more insoluble aluminates and is easy to be stably present in the slurry [20] .

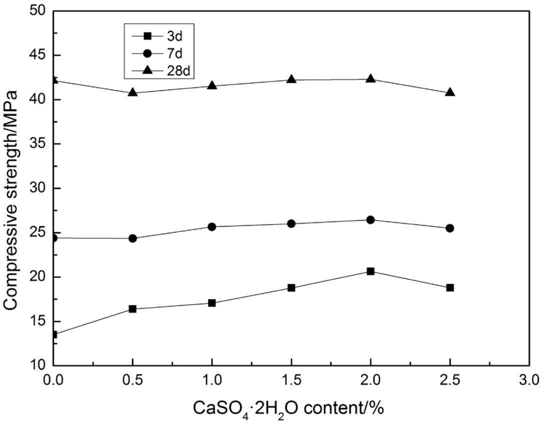


Fig. 3. Compressive strength of steel slag-cement binders with different $CaSO_4\cdot 2H_2O$ contents.

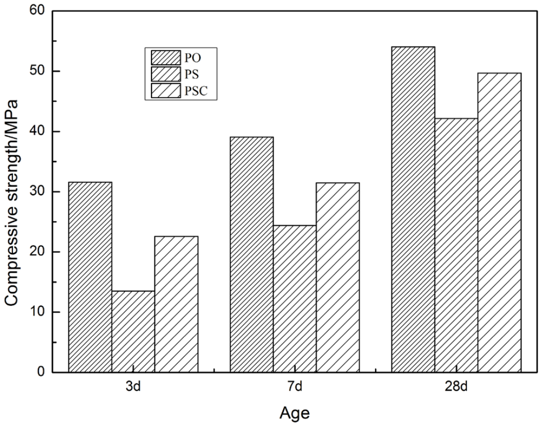


Fig. 4. The compressive strength of three gelling materials at different hydration ages.

3.5 The effect mechanism of steel slag-cement composite materials mixed with $CaCO_3$ and $CaSO_4\cdot 2H_2O$

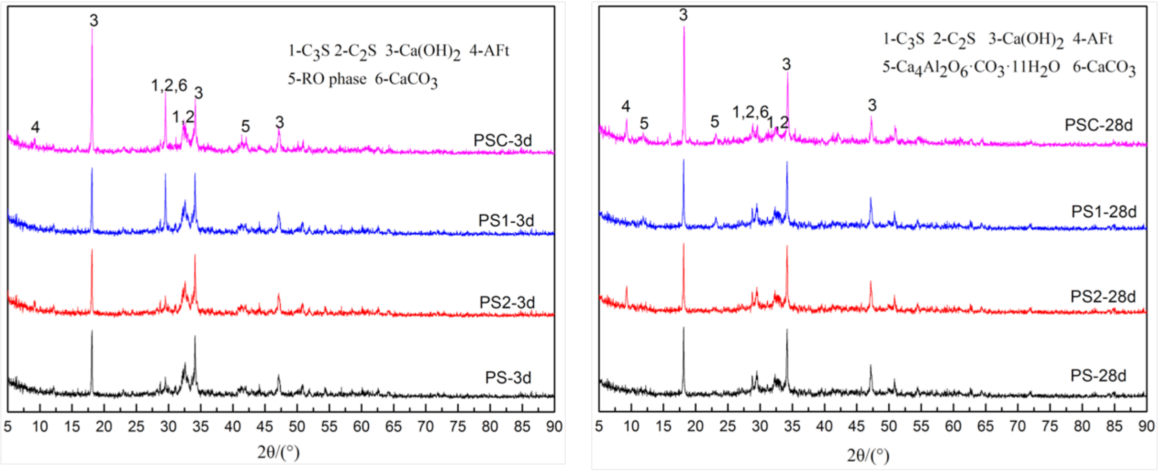
3.5.1 XRD analysis

The XRD analysis of the PS (30% steel slag+70% cement), PS1 (30% steel slag+70% cement+3% $CaCO_3$), PS2(30% steel slag+70% cement+2% $CaSO_4\cdot 2H_2O$) and PSC (30% steel slag+70% cement+3% $CaCO_3$+2% $CaSO_4\cdot 2H_2O$) samples cured for 3 and 28 days are given in Fig. 5. In Fig. 5 (a), the diffraction peak of $Ca(OH)_2$ of PSC-3d is obviously higher than that of PS-3d slurry, which indicates that the incorporation of $CaCO_3$ and $CaSO_4\cdot 2H_2O$ is very efficient to accelerate the early hydration. In addition, the diffraction peak of AFt in PSC-3d slurry is greater than that of PS-3d, illustrating that more ettringite exists in the PSC slurry, which is favorable to the structure of a complex binder. On the whole,in the early hydration stage,the additive of $CaCO_3$ has an obvious influence on the hydration rate, but it has little influence on the species of the hydration products.

When comparing Fig.5 (a) and (b), the intensity of the XRD characteristic peaks of the $CaCO_3$ in PSC-28d is obviously lower than that of the PSC-3d, which suggests that some $CaCO_3$ must have participated in the chemical reaction. As presented in Fig. 5 (b), when cured for 28 days, the PSC slurry generates a new hydration product, that is single-carbon calcium aluminate ($Ca_4Al_2O_6CO_3\cdot 11H_2O$), but the XRD characteristic peaks of the $Ca_4Al_2O_6CO_3\cdot 11H_2O$ have low intensity, because the amount of C_3A in steel slag cement composite paste is low; therefore, only a small amount of single-carbon calcium aluminate is generated.

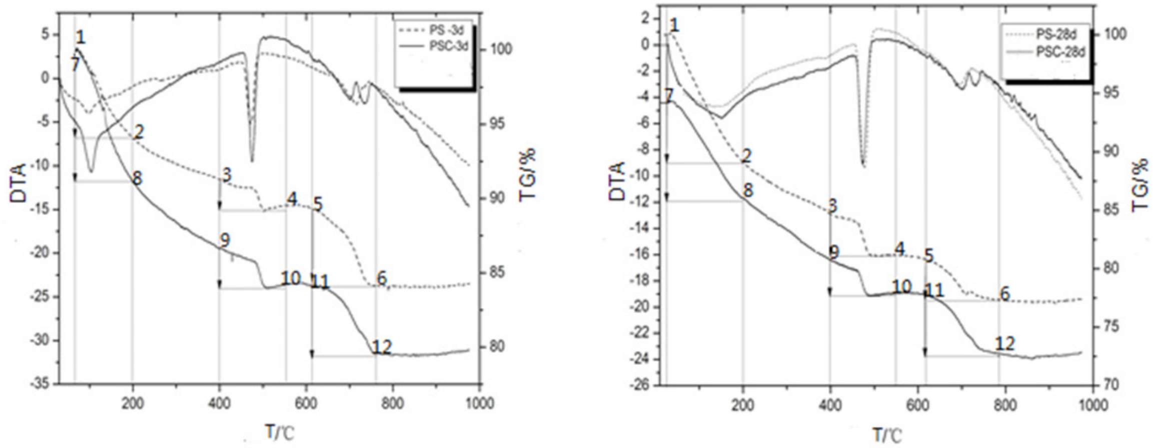
3.5.2 Thermal analysis

Fig. 6 shows the TG-DTA patterns of PS(30% steel slag+70% cement) and PSC(30% steel slag+70% cement+3% $CaCO_3$+2% $CaSO_4\cdot 2H_2O$) hydrated for 3 and 28 days. Generally, the hydration products of cement binding paste have three major endothermic peaks below 1000°C:early dehydration of C-S-H gel and AFt crystals (50°C-200°C); dehydration of $Ca(OH)_2$ (400°C-550°C); later dehydration of C-S-H gel and AFt crystals (600°C-780°C). According to the TG curves in Fig. 6(a), the following can be calculated: from 7 to 8 (50°C - 200°C), the mass loss of PSC-3d is 8.82%, and for PS-3d from 1 to 2 (50°C - 200 °C), the mass loss is 5.91%. From 9 to10 (400°C-550°C), the mass loss of $Ca(OH)_2$ in PSC-3d is 2.66%, whereas in PS-3d, from 3 to 4 (400°C-550°C), the mass loss is 1.74%. From 11 to 12 (600°C-780°C), the PSC-3d mass loss is 5.20%, whereas from 5 to 6 (600°C-780°C), the PS-3d mass loss is 4.62%.



(a) 3d hydration **(b) 28d hydration**

Fig. 5. XRD spectra of PS and PSC hydrated for 3 and 28days(a and b, respectively).



(a) 3d hydration **(b) 28d hydration**

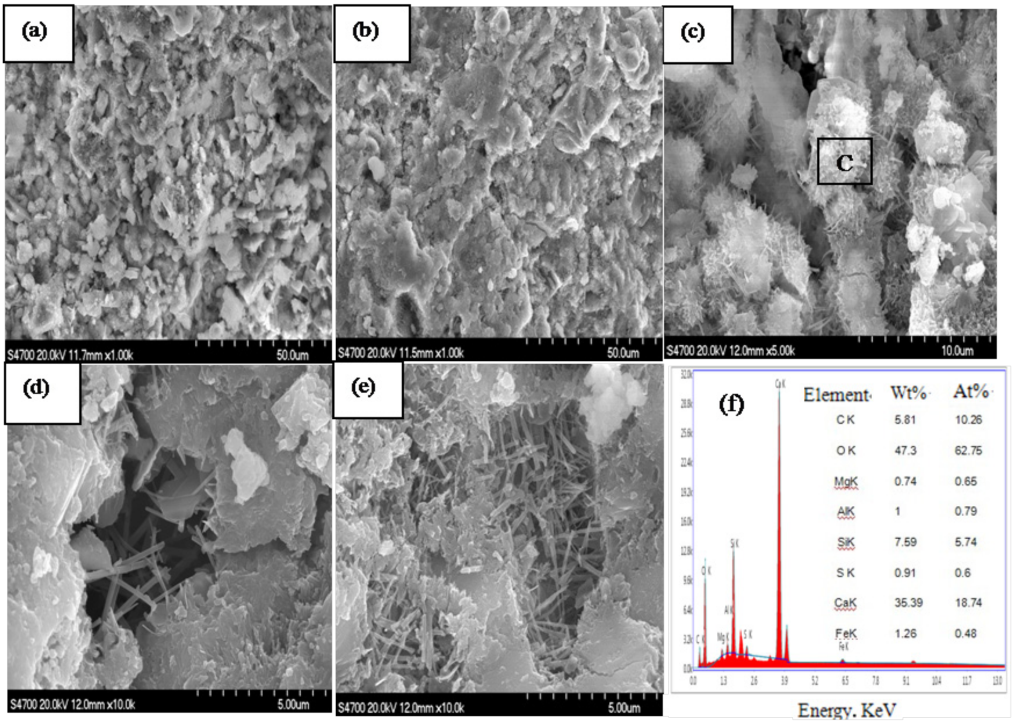
Fig. 6. TG-DTA patterns of PS and PSC hydrated for 3 and 28days(a and b, respectively).

The above analysis shows that each quality loss of PSC-3d is greater than the corresponding PS-3d, illustrating that the number of hydration products of PSC-3d is more than that of PS-3d. Steel slag cement composite materials mixed with $CaCO_3$ and $CaSO_4{\cdot}2H_2O$ can promote slurry to generate more hydration products. The hydration degree of PSC-28d is found to be quite similar to that of PS-28d from Fig. 6(b), but that of PSC-28d is only slightly greater than that of PS-28d. In terms of macro performance, when mixed with $CaCO_3$ and $CaSO_4{\cdot}2H_2O$, the added value of compressive strength at 3 days is greater than that at 28 days.

3.5.3 SEM analysis

Fig.7 shows the microstructure of hydration products of PSC and PS pastes at 3 days. As observed in Fig. 7 (a) and (b), the structure of PS slurry is loose, and many calcium silicate spherical particles have not yet hydrated, whereas the structure of PSC slurry is more compacted. Fig. 7 (c) shows the PSC slurry hydrated for 3 days, the shape of which is clustered. Through EDS analysis, the main elements of the clustered hydration products are C, O, Si and Ca, suggesting that the formation process of C-S-H gel grows not only around the not-hydrated calcium silicate but also around the $CaCO_3$; this is called the "nucleus effect". When the C_3S begin to hydrate and release amounts of Ca^{2+}, these irons are easy to be absorbed on the surface of $CaCO_3$ particles due to physisorption. Subsequently, $Ca(OH)_2$ occurs preferred growth around the $CaCO_3$ particles, thus $CaCO_3$ provides the crystal nucleus and more C-S-H can grow on the surface, resulting in the decrease of the ion concentration in liquid phase, which can accelerate the ion on the surface of the C_3S particles remove to the solution, promoting the early hydration degree of C_3S and improving the early strength of composite binder. Moreover, comparing Fig. 7 (d) with (e), there are more needle stick ettringite crystals (AFt) filled in the gap of the PSC slurry than in PS slurry. AFt can increase the compactness of the slurry and increase the overall strength of the composite slurry.

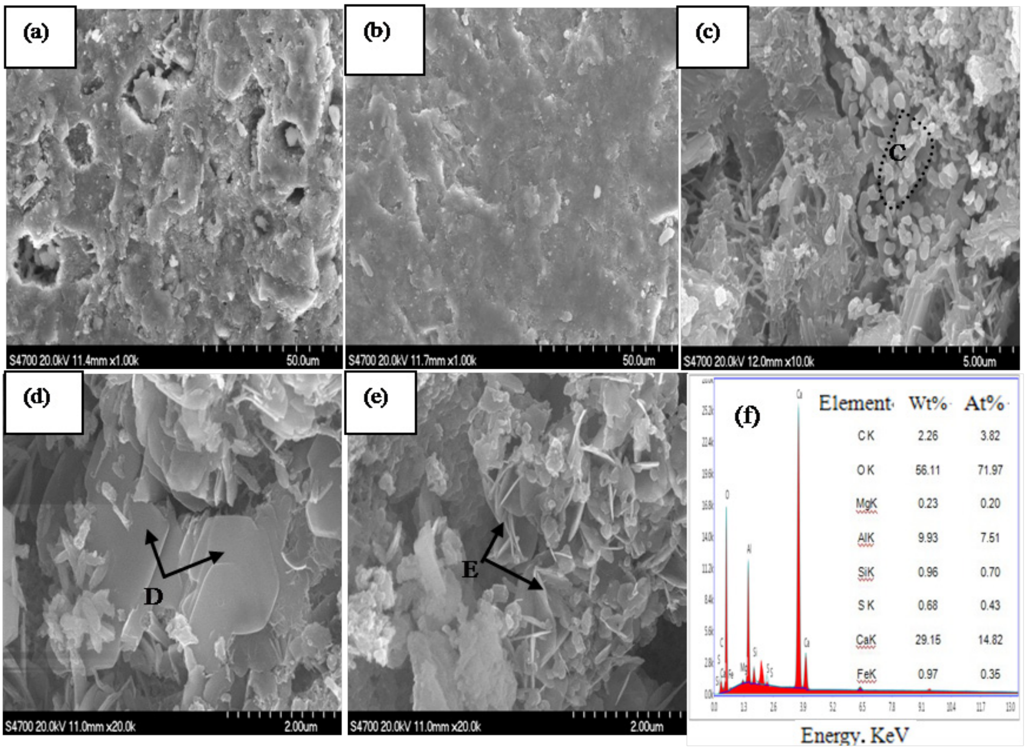
Fig. 8 shows the microstructure of hydration products of the PSC and PS pastes at 28 days. Due to sustainable hydration of cementitious compositions, the whole structure of the



Element	Wt%	At%
CK	5.81	10.26
OK	47.3	62.75
MgK	0.74	0.65
AlK	1	0.79
SiK	7.59	5.74
SK	0.91	0.6
CaK	35.39	18.74
FeK	1.26	0.48

(a) PS-3d (b) PSC-3d (c) PSC-3d (d) PS-3d (e) PSC-3d (f) EDS of point C in (c)

Fig. 7. SEM photos and EDS spectrum of hardened paste hydration for 3d.



Element	Wt%	At%
CK	2.26	3.82
OK	56.11	71.97
MgK	0.23	0.20
AlK	9.93	7.51
SiK	0.96	0.70
SK	0.68	0.43
CaK	29.15	14.82
FeK	0.97	0.35

(a)PS-28d (b) PSC-28d (c) PSC-28d (d) PSC-28d (e) PSC-28d (f) EDS of area C in (c)

Fig. 8. SEM photos and EDS spectrum of hardened paste hydration for 28d.

hardened paste is much denser than that at 3 days. As seen in Fig. 8 (a) and (b), the PSC hardened slurry is more compact than PS obviously. As observed in Fig.8 (d) and (e), some layered materials are found irregularly arranged in the slurry, as indicated by the "D" and "E" arrows. As seen through EDS analysis, this type of hydration product is mainly composed of C, O, Al and Ca , four kinds of elements. Calculated from the proportion of the four elements, the material is closest to the hydration products of single-carbon calcium aluminate ($Ca_4Al_2O_6 \cdot CO_3 \cdot 11H_2O$). As shown in area "C" of Fig. 8 (c), some fine $CaCO_3$ particles, of which the particle size is approximately about 5 µm, filled the gap, thus creating a micro aggregation effect [21] and enhancing the compactness of the cementitious materials.

4 Conclusions

1) $CaCO_3$ can act as the crystal nucleus of hydration products, and thus contribute to accelerating the hydration of C_3S, thereby increasing the early strength of the composite binder. Along with the hydration process, part of the $CaCO_3$ can react with C_3A to generate a new single-carbon calcium aluminate ($Ca_4Al_2O_6 \cdot CO_3 \cdot 11H_2O$), the type of which is layered and irregularly arranged in the slurry. Some unreacted $CaCO_3$ can fill in the cracks of the slurry, creating a micro aggregation effect, which enhances the compactness of the cementitious material.
2) $CaSO_4 \cdot 2H_2O$ can make steel slag-cement complex binders generate more AFt, which can fill in the cracks and increase the strength of the pastes.
3) Both $CaCO_3$ and $CaSO_4 \cdot 2H_2O$ have a significant impact on the macro-performance and microstructure of composite pastes. Compared with the steel slag-cement composite binders without adding $CaCO_3$ and $CaSO_4 \cdot 2H_2O$, the compressive strength increased by 59.9% at 3 days, and by 17.8% at 28 days. The combination of both makes the slurry structure more compact, which is beneficial for increasing the strength of the steel slag-cement composite binders.

Acknowledgements

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